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United States Patent and Trademark Office

May 08, 2003

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.

APPLICATION NUMBER: *10/324,221*
FILING DATE: *December 19, 2002*
RELATED PCT APPLICATION NUMBER: *PCT/US03/10354*

By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS

M. Sias

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Certifying Officer

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12-23-02 [illegible]

12/19/02

UTILITY PATENT APPLICATION TRANSMITTAL
(Large Entity)

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Docket No. 0247.00013
Total Pages in this Submission 29

TO THE ASSISTANT COMMISSIONER FOR PATENTS
Box Patent Application
Washington, D.C. 20231

Transmitted herewith for filing under 35 U.S.C. 111(a) and 37 C.F.R. 1.53(b) is a new utility patent application for an invention entitled:

LIQUID-ASSISTED CRYOGENIC CLEANING

and invented by:

Souvik Banerjee, Harlan Forrest Chung

If a CONTINUATION APPLICATION, claiming benefit of priority of:

☐ **Continuation** ☐ **Divisional** ☐ **Continuation-in-part (CIP)** of prior application No.: **60/369,853**

Which is a:

☐ **Continuation** ☐ **Divisional** ☐ **Continuation-in-part (CIP)** of prior application No.: _____

Which is a:

☐ **Continuation** ☐ **Divisional** ☐ **Continuation-in-part (CIP)** of prior application No.: _____

Enclosed are:

Application Elements

1. ☒ Filing fee as calculated and transmitted as described below
2. ☒ Specification having **13** pages and including the following:
 - a. ☒ Descriptive Title of the Invention
 - b. ☒ Cross References to Related Applications *(if applicable)*
 - c. ☐ Statement Regarding Federally-sponsored Research/Development *(if applicable)*
 - d. ☐ Reference to Sequence Listing, a Table, or a Computer Program Listing Appendix
 - e. ☒ Background of the Invention
 - f. ☒ Brief Summary of the Invention
 - g. ☒ Brief Description of the Drawings *(if filed)*
 - h. ☒ Detailed Description
 - i. ☒ Claim(s) as Classified Below
 - j. ☒ Abstract of the Disclosure

CERTIFICATE OF MAILING BY "EXPRESS MAIL"
"EXPRESS MAIL" Mailing Label Number EV196202680US
Date of Deposit 12/19/02
I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office To Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

Angel Webb
(Signature of person mailing paper or fee)

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UTILITY PATENT APPLICATION TRANSMITTAL
(Large Entity)

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Docket No. 0247.00013
Total Pages in this Submission 29

Application Elements (Continued)

3. ☒ Drawing(s) *(when necessary as prescribed by 35 USC 113)*
 a. ☒ Formal Number of Sheets 2
 b. ☐ Informal Number of Sheets
4. ☒ Oath or Declaration
 a. ☒ Newly executed *(original or copy)* ☐ Unexecuted
 b. ☐ Copy from a prior application (37 CFR 1.63(d)) *(for continuation/divisional application only)*
 c. ☒ With Power of Attorney ☐ Without Power of Attorney
 d. ☐ *DELETION OF INVENTOR(S)*
 Signed statement attached deleting inventor(s) named in the prior application, see 37 C.F.R. 1.63(d)(2) and 1.33(b).
5. ☐ Incorporation By Reference *(usable if Box 4b is checked)*
 The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4b, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.
6. ☐ CD ROM or CD-R in duplicate, large table or Computer Program (Appendix)
7. ☐ Application Data Sheet (See 37 CFR 1.76)
8. ☐ Nucleotide and/or Amino Acid Sequence Submission *(if applicable, all must be included)*
 a. ☐ Computer Readable Form (CRF)
 b. ☐ Specification Sequence Listing on:
 i. ☐ CD-ROM or CD-R (2 copies); or
 ii. ☐ Paper
 c. ☐ Statement(s) Verifying Identical Paper and Computer Readable Copy

Accompanying Application Parts

9. ☒ Assignment Papers *(cover sheet & document(s))*
10. ☐ 37 CFR 3.73(B) Statement *(when there is an assignee)*
11. ☐ English Translation Document *(if applicable)*
12. ☐ Information Disclosure Statement/PTO-1449 ☐ Copies of IDS Citations
13. ☒ Preliminary Amendment
14. ☒ Return Receipt Postcard (MPEP 503) *(Should be specifically itemized)*
15. ☐ Certified Copy of Priority Document(s) *(if foreign priority is claimed)*
16. ☒ Certificate of Mailing
 ☐ First Class ☒ Express Mail *(Specify Label No.):* EV196202680US

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UTILITY PATENT APPLICATION TRANSMITTAL
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Docket No. 0247.00013
Total Pages in this Submission 29

Accompanying Application Parts (Continued)

17. ☐ Additional Enclosures *(please identify below):*

Request That Application Not Be Published Pursuant To 35 U.S.C. 122(b)(2)

18. ☐ Pursuant to 35 U.S.C. 122(b)(2), Applicant hereby requests that this patent application not be published pursuant to 35 U.S.C. 122(b)(1). Applicant hereby certifies that the invention disclosed in this application has not and will not be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication of applications 18 months after filing of the application.

Warning

An applicant who makes a request not to publish, but who subsequently files in a foreign country or under a multilateral international agreement specified in 35 U.S.C. 122(b)(2)(B)(i), must notify the Director of such filing not later than 45 days after the date of the filing of such foreign or international application. A failure of the applicant to provide such notice within the prescribed period shall result in the application being regarded as abandoned, unless it is shown to the satisfaction of the Director that the delay in submitting the notice was unintentional.

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UTILITY PATENT APPLICATION TRANSMITTAL
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Docket No.
0247.00013
Total Pages in this Submission
29

Fee Calculation and Transmittal

CLAIMS AS FILED

For	#Filed	#Allowed	#Extra		Rate	Fee
Total Claims	21	- 20 =	1	x	$18.00	$18.00
Indep. Claims	4	- 3 =	1	x	$84.00	$84.00
Multiple Dependent Claims (check if applicable) ☐						$0.00
					BASIC FEE	$740.00
OTHER FEE *(specify purpose)*	Assignment Recordation					$40.00
					TOTAL FILING FEE	$882.00

☒ A check in the amount of **$882.00** to cover the filing fee is enclosed.

☐ The Commissioner is hereby authorized to charge and credit Deposit Account No. **11-1449** as described below. A duplicate copy of this sheet is enclosed.

- ☐ Charge the amount of as filing fee.
- ☒ Credit any overpayment.
- ☒ Charge any additional filing fees required under 37 C.F.R. 1.16 and 1.17.
- ☐ Charge the issue fee set in 37 C.F.R. 1.18 at the mailing of the Notice of Allowance, pursuant to 37 C.F.R. 1.311(b).

Signature

Dated: **December 19, 2002**

Amy E. Rinaldo, Reg. No. 45,791
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cc:

P01ULRG/REV06

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: SOUVIK BANERJEE, ET AL.

Serial No.: Group Art Unit No.:

Filed: Herewith Examiner:

For: LIQUID-ASSISTED CRYOGENIC CLEANING

Attorney Docket No.: 0247.00013

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Please preliminarily amend the above application prior to consideration of the application on its merits.

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AMENDED VERSION

IN SPECIFICATION:

Page 1, after the Title, please insert the following section:

CROSS-REFERENCE TO RELATED APPLICATIONS

This patent application claims the benefit of priority under 35 U.S.C. Section 119(e) of United States Provisional Serial No. 60/369,853, filed April 5, 2002, which is incorporated herein by reference.

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REMARKS

The above amendment added no new matter and is merely made to more accurately describe and claim the invention, and to claim benefit of priority.

It is respectfully submitted that the application is now in condition for allowance, which allowance is respectfully requested.

Respectfully submitted,

KOHN & ASSOCIATES, PLLC

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Dated: December 19, 2002

CERTIFICATE OF MAILING

EXPRESS MAIL LABEL: EV196202680US

I hereby certify that this correspondence is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231 on December 19, 2002.

Angel Webb

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VERSION SHOWING MARKED CHANGES

IN SPECIFICATION:

Page 1, after the Title, please insert the following section:

--CROSS-REFERENCE TO RELATED APPLICATIONS

This patent application claims the benefit of priority under 35 U.S.C. Section 119(e) of United States Provisional Serial No. 60/369,853, filed April 5, 2002, which is incorporated herein by reference.--

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LIQUID-ASSISTED CRYOGENIC CLEANING

FIELD OF THE INVENTION

[0001] The present invention relates to the use of a liquid, either simultaneously or sequentially, with cryogenic cleaning to aid in the removal of foreign materials, e.g. particles and other contaminants, from semiconductor surfaces, metal films, dielectric films, and other surfaces requiring precision cleaning.

BACKGROUND OF THE INVENTION

[0002] Cleaning or surface preparation of silicon wafers with or without various layers of films is very critical in integrated circuit manufacturing processes. The removal of particles and contaminants from wafer surfaces is performed at several critical process steps during the fabrication of integrated circuits. At a 0.18 μm technology node, 80 out of 400 steps or 20% of the fabrication sequence is dedicated to cleaning. The challenges of cleaning technology are multiplied by the varied types of films, topographies, and contaminants to be removed in front-end-of-line (FEOL) and back-end-of-line (BEOL) cleaning processes. Removal of particles is an important part of this cleaning.

[0003] For the defect-free manufacture of integrated circuits, the International Technology Roadmap for Semiconductors (ITRS) indicates that the critical particle size is half of a DRAM 1/2 pitch [1]. Thus, at the 130 nm technology node, the DRAM 1/2 pitch being 130 nm, the critical particles size is 65 nm. Therefore, particles larger than 65 nm size must be removed to ensure a defect-free device.

[0004] Such small particles are difficult to remove since the ratio of the force of adhesion to removal increases for smaller-sized particles. For submicron particles, the primary force of adhesion of the particles to a surface is the Van der Waals force. This force depends on the size of the particle, the distance of the particle to the substrate surface, and the Hamaker

constant. The Van der Waals force for a spherical particulate on a flat substrate is given as in equation 1:

$$F_{ad} = \frac{A_{132} d_p}{12 Z_0^2} \qquad (1)$$

where A_{132} is the Hamaker constant of the system composed of the particle, the surface and the intervening medium; d_p is the particle diameter; and Z_0 is the distance of the particle from the surface. The Hamaker constant A_{132} for the composite system is given as in equation (2):

$$A_{132} = A_{12} + A_{33} - A_{13} - A_{23} \qquad (2)$$

[0005] The relationship of the Hamaker constant of two dissimilar materials is expressed as the geometric mean of the individual Hamaker constants as $A_{ij} = (A_{ii} * A_{jj})^{1/2}$ where A_{ii} and A_{jj} are the Hamaker constants of materials i and j. It is calculated theoretically using either the Lifshitz or the London models. The Hamaker constant for particles and surfaces used in integrated circuit manufacturing processes is given in literature [2, 3] and is less when the intervening medium is liquid as compared to air. The Van der Waals force, being directly proportional to the Hamaker constant, is therefore reduced when there is a liquid layer between the particle and the surface.

[0006] In addition to the difficulty in removing small particles from the surface, there are various types of organic and metal-organic contaminants which must be cleaned away. As an example, etching is done in integrated circuit device fabrication processes at a number of steps both in FEOL and BEOL to form patterns. The etch is often performed by reactive ion etching (RIE) which generally has a physical and a chemical component to it. Following this process, the etch residues, which are polymeric sometimes with metallic contaminants embedded inside the polymeric matrix, have to be removed. The photoresist film left behind after the etching also has to be removed prior to the next step in the integrated device

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fabrication process. In case of chemical-mechanical polishing, the polishing steps may use Cerria, alumina or silica slurries. After polishing, the slurry and any residues from the slurry additives need to be cleaned from the wafer surface before the next layer of film is deposited. Thus, there is a wide variety of residues, particles and other foreign materials which need to be cleaned both from the surface of the wafer as well as inside any etched features.

[0007] The prior art processes use CO_2 or argon cryogenic sprays for removing foreign materials from surfaces. As examples, see U.S. Patent No. 5,931,721 entitled Aerosol Surface Processing; U.S. Patent No. 6,036,581 entitled Substrate Cleaning Method and Apparatus; U.S. Patent No. 5,853,962 entitled Photoresist and Redeposition Removal Using Carbon Dioxide Jet Spray; U.S. Patent No. 6,203,406 entitled Aerosol Surface Processing; and U.S. Patent No. 5,775,127 entitled High Dispersion Carbon Dioxide Snow Apparatus. In all of the above prior art patents, the foreign material is removed by physical force involving momentum transfer to the contaminants where the intervening medium between particle and substrate surface is air. Since the force of adhesion between the contaminant particles and the substrate is strong, the prior art processes are ineffective for removing small , <0.3 μm, particles.

[0008] U.S. Patent No. 6,332,470, entitled Aerosol Substrate Cleaner, discloses the use of vapor only or vapor in conjunction with high pressure liquid droplets for cleaning semiconductor substrate. Unfortunately, the liquid impact does not have sufficient momentum transfer capability as solid CO_2 and will therefore not be as effective in removing the smaller-sized particles. U.S. Patent No. 5,908,510, entitled Residue Removal by Supercritical Fluids, discloses the use of cryogenic aerosol in conjunction with supercritical fluid or liquid CO_2. Since CO_2 is a non-polar molecule, the solvation capability of polar foreign material is significantly reduced. Also, since the liquid or supercritical CO_2 formation requires high pressure (greater than 75 psi for liquid and 1080 psi for supercritical), the equipment is expensive.

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[0009] As such, there remains a need for a more efficient and effective removal process of contaminants, including particles, foreign materials, and chemical residues, from the surfaces of substrates such as semiconductor wafers, metal films, dielectric films, and other substrates requiring precision cleaning.

SUMMARY OF THE INVENTION

[0010] The present invention provides for a new and improved process for the cleaning of substrate surfaces such as semiconductors and metal and dielectric films to remove contaminants.

[0011] The invention uses a high-vapor pressure liquid prior to cryogenic cleaning to reduce the Van der Waals force of adhesion of the foreign material on the surface. The liquid is sprayed onto the surface and preferably covers the surface for a short period of time. Preferably, the liquid covers the surface for at least one minute. Following this wetting period, the cryogenic spray is initiated. The presence of the liquid will reduce the force of adhesion of the contaminants on the surface thereby making it easier for the particles from the cryogenic spray to dislodge the contaminants from the surface. The liquid may also remove the bulk water from the surface prior to cryogenic cleaning, such as is used in co-pending U.S. patent application 10/215,859 filed on August 9, 2002 and entitled Post CMP Cleaning Using a Combination of Aqueous and Cryogenic Cleaning. The liquid, if chosen with the correct properties, may also dissolve organic contaminants from the substrate surface. The high vapor pressure liquid may be applied simultaneously with the cryogenic cleaning.

BRIEF DESCRIPTION OF THE FIGURES

[0012] Embodiments of the present invention are described with reference to the Figures in which:

Figure 1 is a schematic diagram of the apparatus used in standard CO_2 cryogenic cleaning; and

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Figure 2 is a graph showing the efficiency of particle removal compared to particle size for both standard cryogenic cleaning and the present liquid-assisted cleaning process.

DETAILED DESCRIPTION

[0013] The invention uses liquids having high vapor pressure to reduce the Van der Waals force between foreign material and a substrate surface such as a semiconductor wafer surface or film surface. The high vapor pressure liquid is sprayed on to the surface of the substrate. It is followed with cryogenic cleaning. The initial spraying of liquid will reduce the Van der Waals forces thereby allowing the cryogenic cleaning to more easily remove foreign material from the substrate surface. If the upstream process prior to the cryogenic cleaning is an aqueous based process, as in co-pending U.S. patent application 10/215,859, then the liquid may also remove the bulk water prior to the cryogenic cleaning. Further, the high vapor pressure liquid may act to dissolve organic contaminants from the surface. A particular high-vapour pressure liquid will be chosen depending on the organic contaminants contained on the substrate surface. A skilled person in this field will be aware of the types of liquids which would dissolve common organic contaminants.

[0014] The liquids suitable for use in the present invention have high vapor pressures. Liquids which are suitable for use include, but are not limited to, ethanol, acetone, ethanol-acetone mixtures, isopropyl alcohol, methanol, methyl formate, methyl iodide, ethyl bromide, acetonitrile, ethyl chloride, pyrrolidine, and tetrahydrofuran. However, any liquid having a high vapor pressure may be used. High vapor pressure liquids will readily evaporate off the surface of the substrate without the need for drying by heating or spinning the substrate. The liquids also preferably have low freezing points and are polar in nature. The low freezing point of the liquids ensures that any residual liquid left on the wafer surface at the time of cryogenic cleaning will not freeze due to the drop in wafer temperature that can be attained during the cryogenic cleaning process. The polarity of the liquid aids in the dissolution of organic and inorganic contaminants on the water surface. Preferably, the vapor pressure of the

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liquid is greater than 5 kPa at 25°C, the freezing point of the liquid is below -50°C, and the dipole moment is greater than 1.5 D.

[0015] This process may be used on any substrate surface requiring precision cleaning. These surfaces include semiconductor surfaces as well as metal and dielectric films. Therefore, whenever the term "semiconductor", "metal film", "dielectric film", or "wafer" is used herein, it is intended that the same process may be applied to other substrate surfaces. Other surfaces include hard disk media, optics, GaAs substrates and films in compound semiconductor manufacturing processes. Examples provided herein are not meant to limit the present invention.

[0016] In one embodiment of the present invention, the high-vapor pressure liquid is sprayed onto the surface of a semiconductor wafer at a temperature of 30°-50°C. The liquid may be sprayed either as a thick film or as a thin layer. The layer is preferably at least 5-10 Å thick. It is preferably sprayed using a misting nozzle made of Teflon used in wet benches for spraying deionized water onto wafer surfaces. However, any other nozzle used in the art may be employed. The wafer is preferably covered with the liquid for at least one minute and preferably up to 10 minutes. The liquid may be applied onto the surface once during this time period or it may be sprayed multiple times to ensure that the wafer surface remains wet. As well, the wafer may be rotated at approximately 100 rpm while the liquid is sprayed onto it to ensure uniform coverage of the wafer surface.

[0017] Following this wetting period, the CO_2 cryogenic spraying is initiated. Cryogenic spraying processes may use carbon dioxide, argon or other gases and are well known within the art. Any known technique may be used. The result of the initial high vapor pressure liquid application is the reduction of the Hamaker constant and hence the Van der Waals forces. This application lowers the forces of adhesion of the foreign material to the wafer surface and the foreign material is easier to remove from the wafer surface than through the use of only cryogenic cleaning. It also removes bulk water in a prior aqueous cleaning process.

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[0018] A standard CO_2 cryogenic cleaning process is described in U.S. Patent No. 5,853,962 which is incorporated herein by reference. As an example of a typical CO_2 cryogenic cleaning system, reference is made to Figure 1. The cleaning container 12 provides an ultra clean, enclosed or sealed cleaning zone. Within this cleaning zone is the wafer 1 held on a platen 2 by vacuum. The platen with wafer is kept at a controlled temperature of up to 100°C. Liquid CO_2, from a cylinder at room temperature and 850 psi, is first passed through a sintered in-line filter 4 to filter out very small particles from the liquid stream to render the carbon dioxide as pure as possible and reduce contaminants in the stream. The liquid CO_2 is then made to expand through a small aperture nozzle, preferably of from 0.05" to 0.15" in diameter. The rapid expansion of the liquid causes the temperature to drop resulting in the formation of solid CO_2 snow particles entrained in a gaseous CO_2 stream flowing at a rate of approximately 1-3 cubic feet per minute. The stream of solid and gaseous CO_2 is directed at the wafer surface at an angle of about 30° to about 60°, preferably at an angle of about 45°. The nozzle is preferably positioned at a distance of approximately 0.375" to 0.5" measured along the line of sight of the nozzle to the wafer surface. During the cleaning process, the platen 2 moves back and forth on track 9 in the y direction while the arm of the cleaning nozzle moves linearly on the track 10 in the x direction. This results in a rastered cleaning pattern on the wafer surface of which the step size and scan rate can be pre-set as desired. The humidity in the cleaning chamber is preferably maintained as low as possible, for example <-40°C dew point. The low humidity is present to prevent the condensation and freezing of water on the wafer surface from the atmosphere during the cleaning process which would increase the force of adhesion between the contaminant particles and the wafer surface by forming crystalline bridges between them. The low humidity can be maintained by the flow of nitrogen or clean dry air.

[0019] As well, throughout the cleaning process, it is important that the electrostatic charge in the cleaning chamber be neutralized. This is done by the bipolar corona ionization bar 5. The system also has a polonium nozzle mounted directly behind the CO_2 nozzle for enhancing the charge neutralization of the wafer which is mounted on an electrically grounded platen. The electrostatic charge develops by triboelectrification due to the flow of CO_2 through the nozzle

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and across the wafer surface and is aided by the low humidity maintained in the cleaning chamber.

[0020] For particulate contaminants, the removal mechanism is primarily by momentum transfer of the CO_2 cryogenic particles to overcome the force of adhesion of the contaminant particles on the wafer surface. Once the particles are "loosened", the drag force of the gaseous CO_2 removes it from the surface of the wafer. The cleaning mechanism for organic film contaminants is by the formation of a thin layer of liquid CO_2 at the interface of the organic contaminant and the surface due to the impact pressure of the cryogenic CO_2 on the wafer surface. The liquid CO_2 can then dissolve the organic contaminants and carry it away from the wafer surface.

[0021] Alternatively, the liquid can be applied simultaneously with the CO_2 cryogenic cleaning. In such a case, a second nozzle for spraying the liquid would be mounted in conjunction with a first nozzle used for CO_2 cryogenic cleaning. The liquid would preferably be applied in a thin layer and the CO_2 cryogenic cleaning would continue simultaneously with the spraying of the liquid onto the substrate.

[0022] As a result of the use of the high vapor pressure liquid, the removal of particle contaminants by cryogenic cleaning is significantly improved. Figure 2 shows the efficiency of particle removal compared to particle size for both standard cryogenic cleaning as well as liquid-assisted cryogenic cleaning. Removal of particles having a size below 0.76 μm is significantly improved with the use of the present liquid assisted CO_2 cryogenic cleaning process rather than standard CO_2 cryogenic cleaning. For particle sizes ranging from 0.98 μm to 2.50 μm, there was no significant difference in the removal of particles between the use of the present liquid assisted cryogenic cleaning and the standard CO_2 cryogenic cleaning process.

[0023] The embodiments and examples of the present application are meant to be illustrative of the present invention and not limiting. Other embodiments which could be used in the

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present process would be readily apparent to a skilled person. It is intended that such embodiments are encompassed within the scope of the present invention.

References

[1]. *International Technology Roadmap for Semiconductors* 2001 Edition.

[2]. *Handbook of Semiconductor Wafer Cleaning Technology Science, Technology and Applications*, Edited by Werner Kern, Noyes Publications, 1993.

[3]. *Particle Control for Semiconductor Manufacturing*, Edited by R. P. Donovan, Marcel Dekker Inc., 1990.

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CLAIMS

1. A process for the removal of contaminants from a substrate surface requiring precision cleaning, comprising the steps of: a) applying a high vapor pressure liquid to the substrate surface; and b) cryogenically cleaning the surface of the substrate; to remove contaminants from the substrate surface.

2. The process of claim 1 wherein steps a) and b) are carried out simultaneously.

3. The process of claim 1 wherein the high vapor pressure liquid has a vapor pressure greater than about 5 kPa at 25°C, and a freezing point below about -50°C.

4. The process of claim 3 wherein the high vapor pressure liquid has a dipole moment of greater than about 1.5 D.

5. The process of claim 1 wherein the high vapor pressure liquid is selected from the group consisting of ethanol, acetone, ethanol-acetone mixtures, isopropyl alcohol, methanol, methyl formate, methyl iodide, ethyl bromide, acetonitrile, ethyl chloride, pyrrolidine, tetrahydrofuran and mixtures thereof.

6. The process of claim 1 wherein the substrate is a semiconductor or dielectric film.

7. The process of claim 1 wherein the high vapor pressure liquid remains on the surface in a layer of at least 5 Å for between about 1 to 10 minutes prior to the initiation of cryogenic cleaning.

8. The process of claim 1 wherein the substrate may be rotated during the spraying of the high vapor pressure liquid on the substrate surface.

9. The process of claim 1 wherein the contaminants are less than 0.76 μm in size.

10. The process of claim 1 wherein the high vapor pressure liquid removes bulk water from the surface.

11. A process of cleaning the surface of a semiconductor or dielectric film comprising the steps of: a) spraying a high vapor pressure liquid onto the surface; b) spraying a liquid CO_2 stream through a nozzle to form a gaseous CO_2 stream having solid CO_2 particles, and c) directing said stream at the surface; thereby removing contaminants from the surface.

12. The process of claim 11 wherein the high vapor pressure liquid is sprayed as a mist from a nozzle placed behind a CO_2 nozzle and is sprayed simultaneously with the CO_2.

13. The process of claim 11 wherein the high vapor pressure liquid has a vapor pressure greater than about 5 kPa at 25°C, and a freezing point below about -50°C.

14. The process of claim 13 wherein the high vapor pressure liquid has a dipole moment greater than about 1.5 D.

15. The process of claim 11 wherein the high vapor pressure liquid removes bulk water from the surface.

16. The process of claim 11 wherein the high vapor pressure liquid is selected from the group consisting of ethanol, acetone, isopropyl alcohol, methanol, methyl formate, methyl iodide, ethyl bromide, acetonitrile, ethyl chloride, pyrrolidine, tetrahydrofuran, and mixtures thereof.

17. The process of claim 11 where the gaseous CO_2 stream is directed at the surface at an angle of between 30°-60°.

18. The process of claim 11 wherein the high vapor pressure liquid is sprayed onto the surface as thin layers of at least 5 Å.

19. The process of claim 11 wherein the particles are less than about 0.76 μm in size.

20. A process for cleaning a surface of a semiconductor or dielectric film to remove contaminants having a particle size of about 0.76 μm or less, comprising the steps of: a) spraying a high vapor pressure liquid, having a vapor pressure of 5kPa or greater and a freezing point of about -50°C or less, in thin layers onto the surface; b) leaving the liquid on the surface for at least one minute, prior to the initiation of cryogenic cleaning of the surface.

21. A process for cleaning a surface of a semiconductor or dielectric film to remove contaminants having a particle size of about 0.76 μm or less, comprising the steps of: a) spraying a high vapor pressure liquid, having a vapor pressure of 5kPa or greater and a freezing point of about -50°C or less, in thin layers onto the surface; simultaneously with cryogenic cleaning of the surface.

ABSTRACT

The present invention is directed to the use of a high vapor pressure liquid prior to or simultaneous with cryogenic cleaning to remove contaminants from the surface of substrates requiring precision cleaning such as semiconductors, metal films, or dielectric films. A liquid suitable for use in the present invention preferably has a vapor pressure above 5 kPa and a freezing point below -50°C.

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Docket No.
0247.00012

Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled
LIQUID-ASSISTED CRYOGENIC CLEANING

the specification of which

(check one)

☒ is attached hereto.

☐ was filed on _____ as United States Application No. or PCT International Application Number _____
and was amended on _____
(If applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)			Priority Not Claimed
_____ (Number)	_____ (Country)	_____ (Day/Month/Year Filed)	☐
_____ (Number)	_____ (Country)	_____ (Day/Month/Year Filed)	☐
_____ (Number)	_____ (Country)	_____ (Day/Month/Year Filed)	☐

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I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

60/369,853	04/05/02
(Application Serial No.)	(Filing Date)
(Application Serial No.)	(Filing Date)
(Application Serial No.)	(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. *(list name and registration number)*

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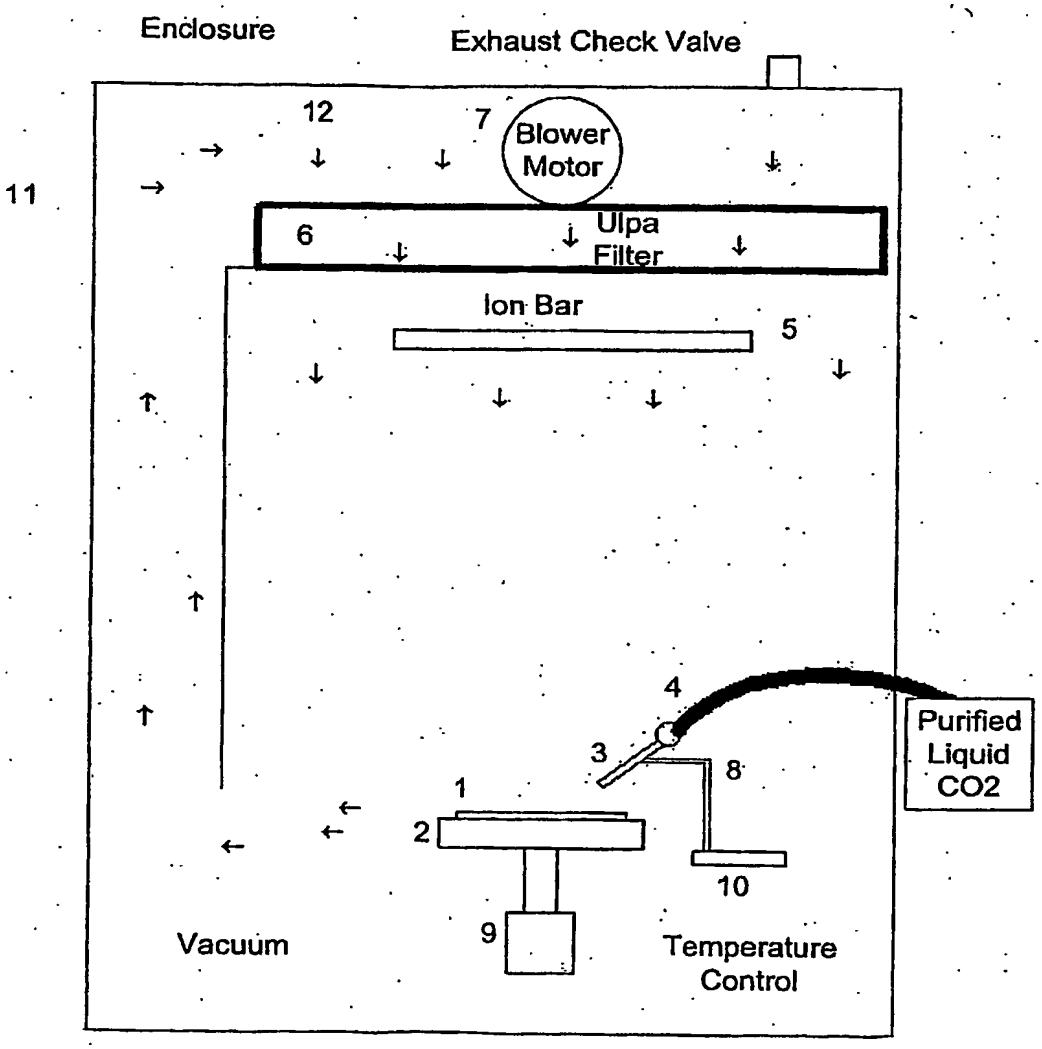


FIG. 1

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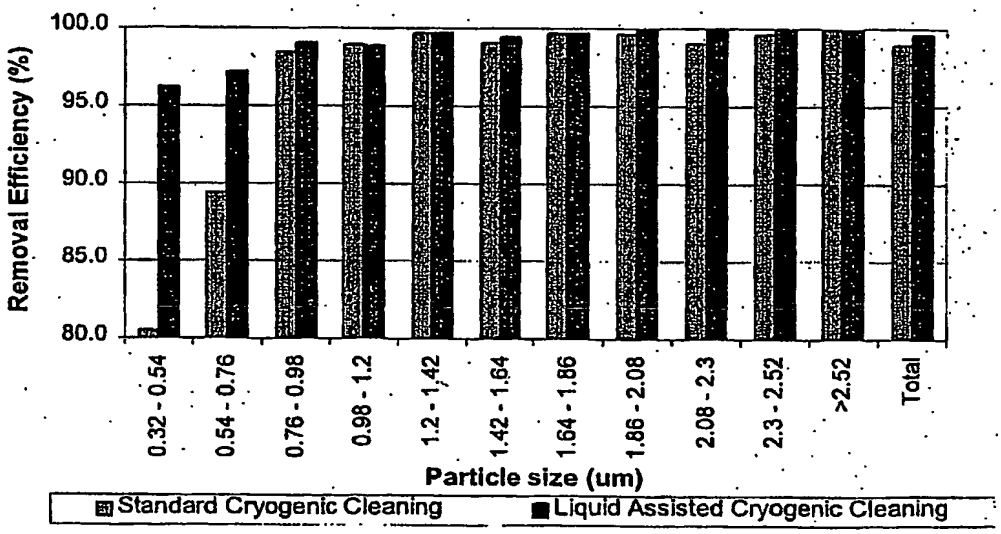


FIG. 2

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